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14. ABSTRACT
This is the final technical report for a three-year project to study growth and characterization of $ZnGeP_2$ and $CdGeAs_2$, and related chalcopyrite crystals. In this project, we have investigated the variety of behaviors exhibited by donors and acceptors in these nonlinear optical materials. The experimental techniques used to characterize the crystals were optical absorption, visible/near-infrared/infrared photoluminescence, electron paramagnetic resonance (EPR), photoinduced EPR, electron-nuclear double resonance (ENDOR), and Hall measurements. Our industrial partner was BAE Systems (formerly Sanders) in Nashua, NH. Specific results during this project include (1) a detailed characterization of the photoinduced optical absorption in $ZnGeP_2$, (2) a comprehensive survey of the PL, optical absorption, EPR, and ENDOR of copper acceptors in $ZnGeP_2$, (3) an EPR, ENDOR, and optical absorption study of nickel in $AgGaSe_2$, (4) a correlation study between PL, EPR, and optical absorption in $CdGeAs_2$, and (5) a study of the effects of Group VI donors (S, Se) in $ZnGeP_2$.

15. SUBJECT TERMS
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FINAL TECHNICAL REPORT
(For project period from May 1, 1999 to April 30, 2002)

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I. Project Overview

This document is the final technical report for work performed under Air Force Office of Scientific Research (AFOSR) Grant F49620-99-1-0248. The report covers the entire three period of the project. The title of the project is "Development of Ternary Chalcopyrite Crystals for High-Power Mid-Infrared Lasers" and the Principal Investigators are Larry E. Halliburton and Nancy C. Giles, Physics Department, West Virginia University. In this three-year research program, which started May 1, 1999, studies to identify and characterize device-limiting point defects in single-crystals of $ZnGeP_2$ and $CdGeAs_2$ were emphasized. These are the materials of choice for high-power, frequency-conversion applications in the mid-infrared region of the spectrum. These crystals have large nonlinear coefficients and sufficient birefringence for phase matching, thus making them excellent choices for tunable laser sources operating in the 3 to 16 μm region. The Air Force has significant interest in developing these materials for use in directed infrared countermeasure systems.

A primary focus of this project has been to determine the variety of behaviors exhibited by donors and acceptors in $ZnGeP_2$ and $CdGeAs_2$. A systematic study of impurities and native defects in these two nonlinear optical materials has been performed during the three-year project period. The experimental techniques used to characterize the crystals included optical absorption, photoluminescence (PL), EPR, photoinduced EPR, ENDOR, and Hall measurements. This project has been conducted in close cooperation with crystal growers and laser-development personnel at BAE Systems (formerly Sanders, Nashua, NH), and the scientific staff at the Air Force Research Laboratory (Dayton, OH). As a result of this project, six students will have received their PhD in Physics, ten refereed papers will have been published in the scientific literature, and seven presentations have been made to the scientific community.

II. Students, Publications, and Presentations

Graduate Students:

During this project, two or three PhD graduate students were supported each year. Among these students, the following have either received their PhD in Physics (or will in the near future).

1. Kevin Stevens (PhD, December 1999)
2. Corneliu Rablau (PhD, December 1999)
3. Nelson Garces (PhD, December 2000)
4. Madalina Chirila, (PhD, expected December 2003)
5. Lijun Wang, (PhD, expected December 2003)
6. Lihua Bai . (PhD, expected December 2004)

Publications Citing Support from this Project:

1. "Characterization of Defect-Related Optical Absorption in $ZnGeP_2$," S. D. Setzler, P. G. Schunemann, T. M. Pollak, M. C. Ohmer, J. T. Goldstein, K. T. Stevens, L. E. Halliburton, and N. C. Giles, Journal of Applied Physics 86, pp. 6677-6681 (1999).

2. "Broad-Band Photoluminescence from $ZnGeP_2$," M. Moldovan and N. C. Giles, Journal of Applied Physics 87, pp. 7310-7315 (2000).

3. "Photoinduced Changes in the Charge States of Native Donors and Acceptors in $ZnGeP_2$," K. T. Stevens, N. C. Giles, L. E. Halliburton, S. D. Setzler, P. G. Schunemann, and T. M. Pollak, Materials Research Society Proceedings, Vol. 607, pp. 379-384 (2000).

4. "Photoluminescence and EPR of Phosphorus Vacancies in $ZnGeP_2$," M. Moldovan, K. T. Stevens, L. E. Halliburton, P. G. Schunemann, T. M. Pollak, S. D. Setzler, and N. C. Giles, Materials Research Society Proceedings, Vol. 607, pp. 445-450 (2000).

5. "Sharp-Line Luminescence and Absorption in $ZnGeP_2$," C. I. Rablau and N. C. Giles, Journal of Applied Physics 90, 3314-3318 (2001).

6. "Luminescence Associated with Copper in $ZnGeP_2$," Lijun Wang, Lihua Bai, K. T. Stevens, N. Y. Garces, N. C. Giles, S. D. Setzler, P. G. Schunemann, and T. M. Pollak, Journal of Applied Physics 92, 77-81 (2002).

7. "Electron Paramagnetic Resonance and Electron-Nuclear Double Resonance Study of the Neutral Copper Acceptor in $ZnGeP_2$ Crystals," K. T. Stevens, L. E. Halliburton, S. D. Setzler, P. G. Schunemann, and T. M. Pollak, Journal of Physics: Condensed Matter 15, 1625-1633 (2003).

8. "Infrared Absorption Bands Related to Native Defects in $ZnGeP_2$," N. C. Giles, Lihua Bai, M. M. Chirila, N. Y. Garces, K. T. Stevens, P. G. Schunemann, S. D. Setzler, and T. M. Pollak, Journal of Applied Physics 93, 8975-8981 (2003).

9. "Optical and EPR Study of Defects in Cadmium Germanium Arsenide," Lihua Bai, N. Y. Garces, Nanying Yang, P. G. Schunemann, S. D. Setzler, T. M. Pollak, L. E. Halliburton, and N. C. Giles, Materials Research Society Proceedings, Vol. 744, 537-542 (2003).

10. "Electron-Nuclear Double Resonance Investigation of Ni^+ Ions in $AgGaSe_2$," K. T. Stevens, L. E. Halliburton, S. D. Setzler, P. G. Schunemann, and T. M. Pollak, Journal of Physics: Condensed Matter (to be submitted in October, 2003).

Presentations Citing Support from this Project:

1. "Photoinduced Changes in the Charge States of Native Donors and Acceptors in $ZnGeP_2$," K. T. Stevens, N. C. Giles, L. E. Halliburton, S. D. Setzler, P. G. Schunemann, and T. M. Pollak, Fall Meeting of the Materials Research Society, Symposium on "Infrared Applications of Semiconductors III", Boston, MA (December 2, 1999).

2. "Photoluminescence and EPR of Phosphorus Vacancies in $ZnGeP_2$," M. Moldovan, K. T. Stevens, L. E. Halliburton, P. G. Schunemann, T. M. Pollak, S. D. Setzler, and N. C. Giles, Fall Meeting of the Materials Research Society, Symposium on "Infrared Applications of Semiconductors III", Boston, MA (November 30, 1999).

3. "Defense-Related Research on Optical Materials Used in Laser Applications," L. E. Halliburton and N. C. Giles, 30-minute presentation, West Virginia EPSCoR State Conference, Charleston, WV (February 15, 2000).

4. "Optical Properties of Copper Doped $ZnGeP_2$," Lijun Wang, Lihua Bai, K. T. Stevens, N. C. Giles, S. D. Setzler, P. G. Schunemann, and T. M. Pollak, poster presentation at the American Conference on Crystal Growth and Epitaxy (ACCGE-13), Burlington, VT (August 12-16, 2001).

5. "Optical Characterization of Ternary Chalcopyrites: $ZnGeP_2$ and $CdGeAs_2$," N. C. Giles, invited presentation at the American Conference on Crystal Growth and Epitaxy (ACCGE-13), Burlington, VT (August 12-16, 2001).

6. "Defects in Ternary Chalcopyrites: Present Status," Nancy C. Giles and Larry E. Halliburton, seminar talk presented at the Physics Department, Northwestern Univ., Chicago, IL (Aug 25, 2001).

7. "Optical and EPR Study of Defects in Cadmium Germanium Arsenide," Lihua Bai, N. Y. Garces, Nanying Yang, P. G. Schunemann, S. D. Setzler, T. M. Pollak, L. E. Halliburton, and N. C. Giles; poster presented at the 2002 Fall Meeting of the Materials Research Society, Boston, MA (Dec 2-6, 2002).

III. Highlights of Research Results

A. Origin of Near-Infrared Optical Absorption in $ZnGeP_2$ (or ZGP)

A broad optical absorption band with peak at room temperature near 1 micron was shown to correlate with the intensity of an EPR signal due to singly ionized zinc vacancies. Our prior work (supported by previous AFOSR funding) has established the primary point defects in ZGP as being zinc vacancies, phosphorus vacancies, and germanium-on-zinc antisites. The first of these acts as an acceptor, while the latter two act as donors in this material. These samples are highly compensated. Our study of samples obtained from 13 different growth runs established the key role that zinc vacancies play in optical absorption.

Using lasers at 633 nm, 1064 nm, and 1.9 microns, a correlation between photo-induced changes in EPR intensity of the three native defects in ZGP and the photo-induced changes in absorption were made. The 633-nm output (from a He-Ne laser) was shown to increase the number of singly ionized zinc vacancies (converting neutral and doubly ionized centers temporarily to the paramagnetic form), and also to convert the two native donors to their paramagnetic form (by temporarily trapping an electron). A quite different set of photo-induced EPR results were obtained using the longer wavelength lasers. By comparing the photo-induced changes in absorption created using these three separate wavelengths, we have been able to assign absorption bands to transitions involving the primary defects. Our results were that the broad 1-micron band is actually composed of two separate absorptions. One absorption peaking near 1.2 microns is an intracenter transition of the singly ionized zinc vacancy. A second broad absorption centered closer to 1 micron is an acceptor-to-donor transition involving the zinc vacancy acceptors and the phosphorus vacancy donors. The photo-induced changes in EPR gave direct support for this assignment. A third and highly polarized absorption near 2.2 microns represents the discrete transition from the valence band to the singly ionized zinc vacancy, i.e., this absorption represents the $V_{Zn}^{-/=}$ transition near 0.6 eV.

We have also determined the origin of a spectrally broad pump-induced absorption in the 1.5-4 micron region. This absorption occurs whenever phosphorus vacancies are converted from

their ionized to their neutral charge state. The absorption represents the electronic transition from a neutral donor (i.e., P vacancy) to the conduction band(s) (the lowest two conduction bands are separated by only 0.15 eV). The P vacancy donor level is found to be about 0.5 eV below the conduction band. The band gap of ZGP is about 2 eV, so this donor is rather deep. We also determined during the course of this project the positions of impurity donor levels due to sulphur and selenium at about 0.3 eV below the conduction band.

B. Photoluminescence of $ZnGeP_2$ (or ZGP)

Most bulk crystals of ZGP obtained from BAE Systems exhibit a broad luminescence band extending from about 1.1 eV to 1.6 eV. We determined that this broad emission is composed of two primary bands. These bands have different polarization dependences, and thus one can change the relative intensities of the two contributions by detecting emission with either $\boldsymbol{E} \parallel c$ or $\boldsymbol{E} \perp c$. In addition, the two bands have quite different excitation power and temperature behaviors. At 5 K, these two bands peak near 1.58 eV and 1.36 eV. The relative intensity of the higher energy band was enhanced in samples that had appreciably more phosphorus vacancies (as determined using EPR). In addition, we performed photoluminescence excitation measurements of ZGP and found that the higher energy band has a resonance when pumping about 90 meV below the minimum conduction band. This resonance is most likely associated with the V_P^- state, which is much shallower than the V_P^0 state at 0.5 eV below the conduction band.

Above 100 K, the 1.58 eV band is thermally quenched (activation energy of 45 meV) and the lower energy emission is the only observable signal (activation energy of 220 meV). Photoluminescence excitation spectra recorded when monitoring this lower-energy band showed discrete sharp resonances near the band edge (2 eV) associated with excitonic absorptions.

In the course of our study, we did observe in some samples a series of sharp emission and absorption lines in the spectral region near 1.7 to 1.8 eV. Two sharp zero-phonon lines with opposite polarizations are resolved in emission at 1.7849 eV (at 70 K) and 1.7784 eV (at 5 K). Thermalization occurs between these two lines, suggesting a split excited state of the center. Broad phonon structure was also observed with local-mode energies of 6.3 meV, 7.3 meV, and 43.7 meV. Similar spectra are observed in absorption. These structured spectra are explained by a model of radiative recombination of excitons bound to an isoelectronic defect center in a tetragonal lattice. The observed polarization behavior is produced by the built-in distortion along the c axis associated with the chalcopyrite structure. The specific defect model could not be determined, only that it was an isoelectronic defect.

C. Role of Copper in $ZnGeP_2$

Copper, substituting for zinc, is expected to provide an acceptor level in $ZnGeP_2$. However, Cu is known to exist in two different stable forms when incorporated on a group II site in solids. For example, Cu^{2+} in ZnS and ZnSe is in a stable $3d^9$ configuration and is not a suitable electrically active acceptor. In the smaller band-gap materials, such as CdTe and ZnTe, Cu is observed to act as an acceptor. If a similar behavior was produced in ZGP, adding the Cu impurity to the lattice could thus lead to the elimination of absorption bands associated with the singly ionized Zn vacancy (a very important result for optimizing infrared countermeasure device performance), if the Cu acceptor were a shallow level. There have been no reports of EPR spectra from isolated copper acceptors in ZnS, ZnSe, ZnTe, CdTe, and GaP (the binary analog to ZGP). We completed investigations of two types of copper-doped $ZnGeP_2$ crystals, those having copper incorporated during growth and those having copper diffused in after growth (i.e., in post-growth anneals). We have used EPR, ENDOR, PL, and optical absorption spectroscopies to determine the effects of copper doping on ZGP bulk crystals. The lack of previous results on EPR of neutral copper acceptors gives this work added importance.

In ZGP, our EPR and ENDOR study proves that doping with copper in the melt at levels of parts per million can produce behaviors of a conventional acceptor. Because of compensation due to native donors, the copper acceptors exist in their nonparamagnetic, singly ionized charge state (Cu_{Zn}^-). The paramagnetic neutral charge state can be photoinduced. The g matrix of the neutral copper acceptor is axial ($g_{\parallel} = 2.049$ and $g_{\perp} = 2.030$), with the unique principal direction parallel to the tetragonal *c* axis of the crystal. The hyperfine and nuclear quadrupole matrices also exhibit c-axis symmetry. Equal hyperfine interactions with the four nearest-neighbor phosphorus ions are well resolved in the c-axis EPR spectrum.

Photoluminescence and absorption measurements of the copper-doped ZGP samples were completed. At 5 K, the copper doped samples all exhibit a new emission band at 1.3 eV. This emission band is strikingly different from the broad PL detected from undoped samples (described in section B. above). The new band is not strongly polarized and has a thermal quenching activation energy of 0.12 eV. Photoluminescence excitation data and optical quenching data support an assignment to this 1.3-eV emission band of donor-acceptor pair recombination between a 0.12-eV donor and a 0.6-eV acceptor, i.e., copper. Low-temperature absorption data taken from the series of copper-doped samples revealed enhanced absorption peaking near 0.6 eV for heavily doped samples produced by diffusion anneals.

D. EPR and ENDOR of Phosphorus Vacancy in $ZnGeP_2$

A complete angular dependence of the EPR signal from the neutral phosphorus vacancy in ZGP was measured. A sample was chosen for this work that had a large photoinduced EPR signal, thus allowing us to improve the precision of the g value measurements. ENDOR data was also taken from the phosphorus vacancy. A large number of weakly coupled phosphorus interactions were observed. The ENDOR measurements required the use of an optical fiber to transmit the laser beam into the microwave cavity (since the ENDOR cavity did not allow direct optical access through side-wall slots).

E. EPR and Optical Correlation Study in $CdGeAs_2$

One of the limitations presently restricting use of $CdGeAs_2$ in nonlinear optical devices operating in the infrared is a room-temperature optical absorption peaking near 5.5 microns. Upon sample cooling, the absorption decreases. This absorption has been attributed to inter-valence band transitions and is associated with the presence of a shallow acceptor. We have completed a study of over 50 CGA crystals (from BAE Systems) representing a wide range of 5.5 micron absorption intensities. We used EPR, Hall, optical absorption, and infrared PL to study the crystals. We found that an EPR signal near $g = 2$ is largest in crystals which have large 5.5-micron absorptions. Our study included samples with absorption at 5.5 microns (the discrete band only) varying from about 0.1 cm^{-1} to 10 cm^{-1}. The associated EPR signal intensity for absorption of 0.1 cm^{-1} corresponds to a defect concentration of about 10^{18} cm^{-3}. Identification of the paramagnetic defect responsible for the EPR spectrum is very important. We performed EPR lineshape simulations and proposed that the shallow acceptor defect is most likely the Ge-on-As antisite.

From our study, we have correlated the emission intensity of PL with the optical absorption. Typical reports of PL from bulk crystals of CGA show two emission bands near 0.55 eV and 0.35 eV. The energy position of the highest energy band varies from sample-to-sample. We find that the higher energy emission band is completely absent in some crystals that show no or little of the intervalence-band absorption. We attributed this higher energy emission to the shallow acceptor defect. Even in the best samples studied, we find the lower energy band is still present. Thus, the major limitation to device-quality CGA is the shallow, not deeper, acceptor. We also completed a correlation study between room-temperature Hall carrier concentration and absorption for these samples from BAE Systems.

F. Role of Nickel in $AgGaSe_2$

EPR and ENDOR studies have been performed on $AgGaSe_2$ crystals grown by the horizontal-gradient-freeze technique. An impurity defect has been characterized and identified

as a Ni^{+} ion substituting for a Ag^{+} ion. This nickel defect exists in as-grown crystals in the paramagnetic state. A complete ENDOR angular dependence study provided spin-Hamiltonian parameters for the ^{61}Ni isotope as well as the neighboring selenium ions (^{77}Se) and gallium ions (^{69}Ga and ^{71}Ga). Optical absorption data taken at room temperature and liquid-helium temperature (10 K) showed a broad band peaking near 2.2 microns. The zero-phonon line position was determined from the 10-K data. The EPR and optical absorption data were consistent with each other, suggesting the absorption band was associated with Ni^{+} impurities. Samples containing higher doping levels of nickel exhibited larger Ni EPR intensity and larger absorption. We also have observed Ni^{3+} in samples containing only trace amounts of nickel. In these lighter dopings (unintentional), a photo-induced change in EPR intensity of the Ni^{+} and Ni^{3+} spectra was observed.